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### Abstract

Artificial filaments, foils and similar articles which swell or dissolve in water are produced by extruding into a setting medium a solution of a polyvinyl ester containing free hydroxyl groups in which the ester group content is between 2 and 12 per cent of the maximum theoretically possible. The setting medium may comprise a water-miscible organic non-solvent for the ester, such as acetone or lower aliphatic ketones or alcohols, and the polyvinyl compound may comprise partially saponified polyvinyl acetate. The solution of polyvinyl ester in cold or hot water may be forced through orifices of 0.05 to 0.08 mm. diameter and the filaments so formed passed through the setting medium for a distance of 6 to 12 feet. After setting the yarn is twisted and wound, but it is preferably first stretched in a steam chamber at 100 DEG C., after which it is allowed to remain on the bobbin for 12 to 24 hours to set. In an example, polyvinyl acetate made by saponifying polyvinyl acetate of 100 per cent acetate content in a medium containing 3 per cent of water and 97 per cent of methyl alcohol at about 50 DEG C. so as to produce a partially saponified polyvinyl acetate containing 11 per cent of the theoretically possible quantity of acetate groups is heated with water until the polyvinyl acetate has dissolved and the methyl alcohol and methyl acetate boiled off. The solution is filtered and spun into acetone at room temperature, the length of immersion being about 10 feet. The yarn produced is immersed in acetone for 12 hours, then stretched to three times its original length while passing through wet steam at 100 DEG C., and finally aged for 24 hours in air. Specifications 482,216 and 563,991 are referred to.

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## PATENT SPECIFICATION

Application Date : Nov. 21, 1942. No. 15050/41.

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Complete Specification Left : Oct. 17, 1942.

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## PROVISIONAL SPECIFICATION.

## Improvements in or relating to the Production of Textile and other Products from Polyvinyl Esters.

We, ROBERT PIERCE ROBERTS, EDGAR BERT JOHNSON and HARRY HECTOR TAYLOR, all British subjects, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention is concerned with improvements in the production of textile and other products from polyvinyl esters.

According to the present invention, artificial filaments which are soluble in water are produced by spinning suitable polyvinyl compounds which are soluble in water.

The preferred method for the production of the water-soluble filaments of the present invention consists in making them directly from a water-soluble polyvinyl compound by spinning a solution of the compound into a coagulating medium. It is preferred to employ a solution of the polyvinyl compound in an aqueous medium, and most advantageously in water, and to spin that solution into an organic medium or a medium consisting largely of an organic liquid. Methyl and ethyl alcohols are not suitable, but ketones, for example acetone or methyl ethyl ketone, or any other organic liquids or mixtures of organic liquids which are non-solvents for the polyvinyl compound and which are miscible with water may be used. Thus, for example, a 15—25% solution of a polyvinyl compound in water may be spun into acetone. After the filaments have been coagulated, they may be dried and wound.

It has been found that the greatest solubility in water is not obtained by complete saponification of a polyvinyl compound, for example polyvinyl acetate, and that there exists a range of values for residual acetyl groups, for example, within which there is an optimum solubility in water. This range depends to a small extent upon the degree of polymerisation of the polyvinyl compound, but in general it appears that in the case of saponifying polyvinyl acetate the best range for the degree of saponification is that in which 5—15% of the theoretical maximum of acetyl groups is retained.

If polyvinyl butyrate is used, for example, the range of residual butyryl groups will be somewhat lower than the figures indicated. However, even where the polyvinyl compound used for spinning is not completely soluble in cold water in the sense that it will not form a clear solution upon attempting to dissolve it in cold water, solution and spinning may be carried out by heating the polyvinyl compound with water to dissolve it, and then either cooling the solution or spinning it while still warm.

The production of the water-soluble polyvinyl compounds is usually effected by saponifying polyvinyl acetate or other saponifiable polyvinyl compound, and since the product has subsequently to be dissolved to form a spinning solution it is preferable to carry out the saponification process also with a medium which will dissolve both the starting material and the water-soluble compound produced. For example polyvinyl acetate may be refluxed with methyl or ethyl alcohol until it is dissolved, after which a solution of caustic soda in methyl or ethyl alcohol is mixed with the polyvinyl acetate solution and saponification effected. When an alcohol is used as the solvent medium it is necessary to employ only a relatively small proportion of the amount of saponifying agent theoretically required to effect the desired degree of saponification. For example an amount of caustic soda equal to 1 or 2% of the weight of polyvinyl acetate is sufficient to effect complete saponification.

As already indicated, the solubility properties of the saponified product are dependent to some extent upon the saponifying conditions employed. In general the best results appear to be obtained by dissolving polyvinyl acetate, for example, in methyl alcohol, and mixing the solution with a solution of the desired amount of caustic soda also in methyl alcohol. 1.25% of caustic soda on the weight of the polyvinyl acetate has given very good results when carrying out the saponification at about 40—50° C. in a total quantity of methyl alcohol of some 2—4 times

the weight of the polyvinyl acetate. To obtain the products referred to above within the range of maximum solubility in cold water, the degree of saponification may be controlled in any desired manner. For example, the saponification may be carried out very slowly at comparatively low temperatures, and stopped at the desired stage. However, a much better control is obtained by controlling the amount of water in the methyl alcohol or similar saponification medium as is described in our application, No. 7297/43 (Serial No. 363,991). It is found that by adjusting this amount of water, a very rigid control is obtained over the nature of the ultimate saponification product. The more water there is present, the higher is the residual acetyl content of the saponified polyvinyl acetate. For the range of residual acetyl groups given above, namely 5—15% of the theoretical maximum, a total content of water of 2—5% on the weight of the methyl alcohol appears to give the best results.

The degree of polymerisation of the polyvinyl compound is also of importance and it should preferably contain 100 or 200 or more polyvinyl residues.

A further important feature of the present invention is obtaining a good tensile strength of the water-soluble polyvinyl filaments. According to the invention, the tensile strength of the filaments as spun is increased by subsequently subjecting them to a stretching operation. This stretching operation may be carried out in air, but is preferably carried out in the presence of a softening agent for the polyvinyl compound. Water is, of course, a

powerful softening agent and, if used, has to be used with caution. In the form of an atmosphere of steam it greatly facilitates the stretching of the filaments, and even an atmosphere of humid air is very advantageous. By these means, stretches of 400—600% or more of the original length of the filaments may be obtained. One specific method which we have found advantageous is to immerse the filaments on bobbins in acetone, and then to pass the filaments from the bobbins through an atmosphere of steam in which they are stretched. After passing through the steam, they are taken up on another bobbin, and allowed to remain on the bobbin under tension for 12 hours or so in order to age them. This subsequent ageing is likewise of some importance in obtaining a stable product of good tensile strength.

An important use of the water-soluble filaments with which the present invention is concerned is for the production of water-soluble fabrics used for parachutes for mines to be laid in rivers or the sea, since after the mines have been laid the parachute dissolves and does not reveal the presence of the mine. Filaments intended for this purpose may be dyed a suitable shade to render the parachute inconspicuous before it dissolves. For instance a dyestuff may be introduced into the spinning solution. The water-soluble compounds may also be used for other purposes, for example, as sizes.

Dated this 21st day of November, 1941.

STEPHENS & ALLEN.

Chartered Patent Agents.

Wykeham House, Gordon Avenue,  
Stanmore, Middlesex.

## COMPLETE SPECIFICATION.

### Improvements in or relating to the Production of Textile and other Products from Polyvinyl Esters.

We, ROBERT PIERCE ROBERTS, EDGAR BERT JOHNSON and HARRY HECTOR TAYLOR, all British subjects, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is concerned with improvements in the production of textile and other materials from polyvinyl esters.

It is known that polyvinyl esters may be saponified partially or completely and that the solubility of the esters in different solvents may be widely varied according to the degree to which the

saponification is carried out. In British Specification No. 482,216 there is described a process in which polyvinyl esters are first saponified to a certain degree and are then shaped, e.g. by extruding solutions thereof into an evaporative medium or a liquid coagulating bath; the degree of saponification is to be such that the products are soluble in organic solvents and substantially insoluble in water; and these requirements are satisfied by a saponified polyvinyl ester which has an ester group content of 60—80% of the maximum theoretically possible.

The present invention, however, aims at the production of shaped articles, e.g. filaments, yarns, foils and the like, which are capable of being swollen or dissolved

by water. by extruding into a settling medium a solution of a polyvinyl ester; to achieve this is necessary that the polyvinyl ester should have the desired sensitivity towards water, and also that the solution should be capable of being shaped by extrusion (or "spun") successfully. We have now found that polyvinyl esters having an ester group content between 2 and 12% are satisfactory starting materials for the production of such articles, both as regards their sensitivity towards water and the spinning properties of their solution.

According to the present invention, therefore, artificial filaments, foils and similar articles which swell or dissolve in water are produced by shaping and setting solutions of polyvinyl esters containing free hydroxyl groups in which the ester group content is between 2 and 12% of the maximum theoretically possible.

Preferably the polyvinyl ester employed contains acetyl groups, although esters containing other groups, e.g. butyl groups, may be used. The degree of polymerisation is preferably such that the polyvinyl ester contains 100 or 200 or more vinyl residues.

The artificial filaments and other articles are preferably produced by extruding an aqueous solution of the polyvinyl ester into a coagulating medium containing a water-miscible organic non-solvent for the ester. Usually a concentration of about 20, 25 or 30% of polyvinyl ester gives a solution having a suitable spinning viscosity. The solution may be prepared by dissolving the polyvinyl ester in cold water or by heating it up with water and, if necessary, the solution may be spun while it is still hot. For the production of filaments, jets having orifices of about 0.05, to 0.08 millimetres diameter are suitable and the solution may be extruded through such jets into a coagulating bath and passed through the bath for a distance, for example, of 6 to 12 feet. The water-miscible organic non-solvents which it is preferred to use are lower aliphatic ketones, particularly acetone, though other such compounds, for example lower aliphatic alcohols, may be employed.

After setting, (and drying if a wet-spinning process is employed) the yarn may be wound or twisted and wound and then employed for the production of fabrics or other articles. It is preferable, however, that it should first be subjected to a stretching operation in order to increase its tenacity. Stretching may be carried out in air, but is preferably effected in the presence of a softening agent for the polyvinyl ester. Water

is, of course, a powerful softening agent and if used must be used with caution. Moist air may, for example, be employed but preferably an atmosphere of steam is used. A very useful method comprises stretching the yarn while it passes through a chamber containing steam, e.g. at a temperature of 100° C., after which it is wound and allowed to remain on the bobbin under tension for 12 to 24 hours in order to set. The degree of stretch may, for example, be 2, 4 or 6 times according to the tenacity and extension required in the final yarn. One specific method which has been found advantageous is to immerse the yarns on bobbins in acetone, and then to pass the yarn from the bobbins through an atmosphere of steam in which they are stretched. After passing through the steam they are taken up on other bobbins and allowed to remain on the bobbins under tension for 12 hours or so in order to age them. This ageing is of some importance in obtaining a stable product of good tensile strength.

The value of the stretching operation is not limited to polyvinyl ester yarns sensitive to water which have been produced as described in the present application, but is applicable to such yarns containing hydroxyl groups and having an ester group content of 2-12%, however they may have been produced.

While the process of the present invention is not confined to the use of polyvinyl esters produced by any particular process it has been found that compounds which have properties rendering them particularly suitable may be obtained by saponifying polyvinyl esters of comparatively high ester group content in solution in a medium comprising an alkali, a lower aliphatic alcohol and not more than 10%, especially between 1 and 4%, of water, calculated on the total weight of liquid present at the commencement of saponification, the amount of alkali being substantially less than that theoretically necessary to effect the desired degree of saponification. It has been found that the degree of saponification and the solubility properties of the polyvinyl ester obtained can be controlled to some extent by adjustment of the amount of water present in the saponification medium, the greater the quantity of water the higher being the ester content of the product obtained. This process is more fully described and claimed in our Specification No. 7297/43 (Serial No. 563,991).

#### EXAMPLE I.

A polyvinyl acetate with an acetate content of 11% of the maximum theoretically possible was made by saponifying

polyvinyl acetate, of approximately 100% acetate content, at about 50° C. in a saponification medium containing 1.25% of caustic soda (calculated on the weight of the polyvinyl acetate) dissolved in aqueous methyl alcohol containing 3 parts by weight of water and 97% parts of methyl alcohol: saponification was continued until the product separated out. This product was introduced while still wet into hot water and the mixture was heated on a water bath until the polyvinyl acetate had dissolved and the methyl alcohol and methyl acetate had boiled off. The amount of polyvinyl acetate used was sufficient to give a solution having a concentration of about 28%. The solution was filtered while warm, after which it was spun into acetone at room temperature, the length of immersion being about 10 feet. The yarn produced was twisted and wound and the bobbins were immersed in acetone for about 12 hours to allow the yarn to age. It was then stretched to about 3 times its original length while passing through a chamber containing wet steam at 100° C., and then aged for 24 hours in air after which it was ready for use in the production of fabrics or other articles. The yarn produced was soluble in cold water.

#### EXAMPLE II.

A polyvinyl acetate was made as described in Example I. except that the saponification medium containing 2½% of water and 97½% of methyl alcohol, with the result that a product of slightly lower acetate content was obtained. Yarn produced therefrom by the process described in Example I did not completely dissolve in cold water, but shrank and sank in the water after immersion.

The saponification process described in the above Examples form part of the subject matter of our Application No. 7297 42 (Serial No. 563,991).

Yarns obtained from polyvinyl esters of ester group content between 2 and 12%, as described in the present application, may be employed for the production of fabrics and may constitute either the whole of such fabrics or may form only part thereof. For example they may be used as weft in conjunction with a warp made of acetone-soluble cellulose acetate. These fabrics, which dissolve or disperse in water, are very useful for the production of parachutes for mines to be laid in rivers or the sea, since after the mines have been laid the parachute becomes

substantially invisible and does not reveal the presence of the mine. Such fabrics may be dyed a suitable shade in order to render the parachute inconspicuous before it dissolves, for instance, by introducing a dyestuff into the spinning solution from which the yarns are produced.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the production of artificial filaments, foils and similar articles, which comprises extruding through a shaping device into a setting medium a solution of a polyvinyl ester containing free hydroxyl groups in which the ester group content is between 2 and 12% of the maximum theoretically possible.

2. Process for the production of artificial filaments, foils and similar articles, which comprise extruding an aqueous solution of a polyvinyl ester containing free hydroxyl groups, in which the ester group content is between 2 and 12% of the maximum theoretically possible, into a coagulating medium comprising a water-miscible organic non-solvent for the ester.

3. Process according to Claim 2, wherein the organic non-solvent is a lower aliphatic ketone.

4. Process according to Claim 2, wherein the organic non-solvent is acetone.

5. Process according to any of the preceding claims, wherein the polyvinyl compound contains vinyl acetate groups.

6. Process for improving the properties of water-sensitive yarns and similar articles made of a polyvinyl ester containing free hydroxyl groups and having an ester group content between 2 and 12% of the maximum theoretically possible, which comprises subjecting said articles to a stretching operation.

7. Process according to Claim 6, wherein stretching is effected in an atmosphere of steam.

8. Filaments, foils and similar articles having a basis of a polyvinyl ester containing free hydroxyl groups which swell or dissolve in water, obtained by any of the processes hereinbefore described or claimed.

Dated this 16th day of October, 1942.

STEPHENS & ALLEN.

Chartered Patent Agents.

Wykeham House, Gordon Avenue.

Stammore, Middlesex.